

Non-halogenated Anti-flammable Polymers prepared from Deoxybenzoin Monomers

NIST Annual Fire Conference April 4,5 2007



***Conte Center for Polymer Research
Univ. of Massachusetts Amherst***

***Funding: Federal Aviation Administration, National Institute for Standards and Technology, U.S. ARMY
corporate sponsors:***

*General Electric Co., International Association of Fire Fighters, Boeing, Johns Manville
Multina, Inc, Rogers Corp., Schneller, Inc., Solvay Advanced Polymers*

Polymer Flammability Effort at UMass Amherst

“Cluster F” of the Center for UMass-Industry Research on Polymers (CUMIRP)

A property-driven research cluster, encompassing the synthesis, characterization, and modeling of polymers, centered on the development of low heat release polymers and polymer composites

Current efforts

Synthesis: Halogen-free anti-flammable polymers

Modeling: pyrolysis kinetics and mechanisms

Processing: Films, Fibers, Electrospinning

Characterization: Flammability (pyrolysis combustion flow calorimetry);
Mechanical properties

Personnel: 5 PIs, 6 students and postdoctoral associates

Characterization Techniques in Cluster F Research

Techniques for evaluating thermal properties on a small scale



Py-GC/MS:

Pyrolysis GC/MS
(1 mg)

- Decomposition products
- Mechanism of decomposition



TGA:

Thermogravimetric
Analysis
(10 mg)

- Thermal stability
- Char yield

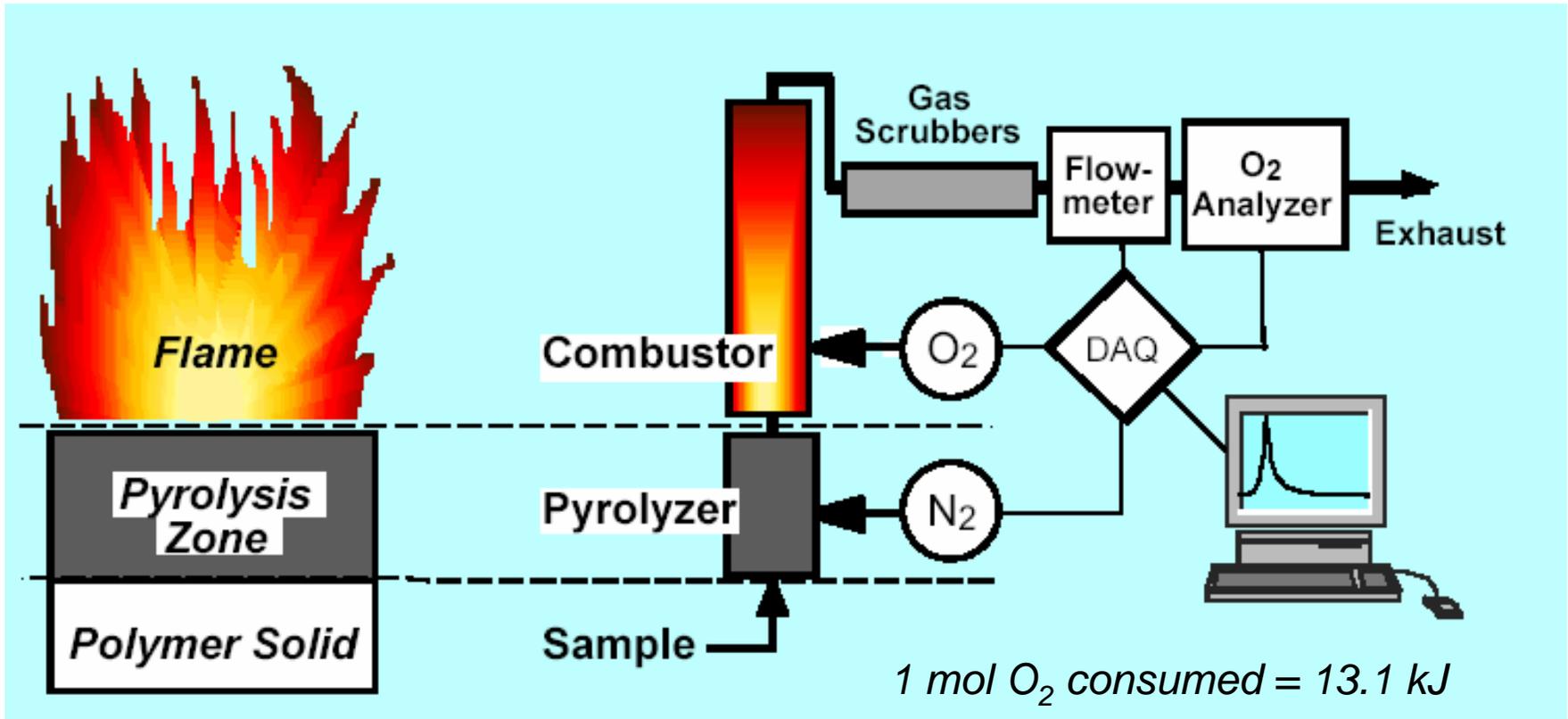


PCFC (FAA):

Pyrolysis-combustion
flow calorimeter
1 mg samples!!!

- **Heat release capacity**
- Total heat of combustion
- Char yield

Pyrolysis Combustion Flow Calorimetry



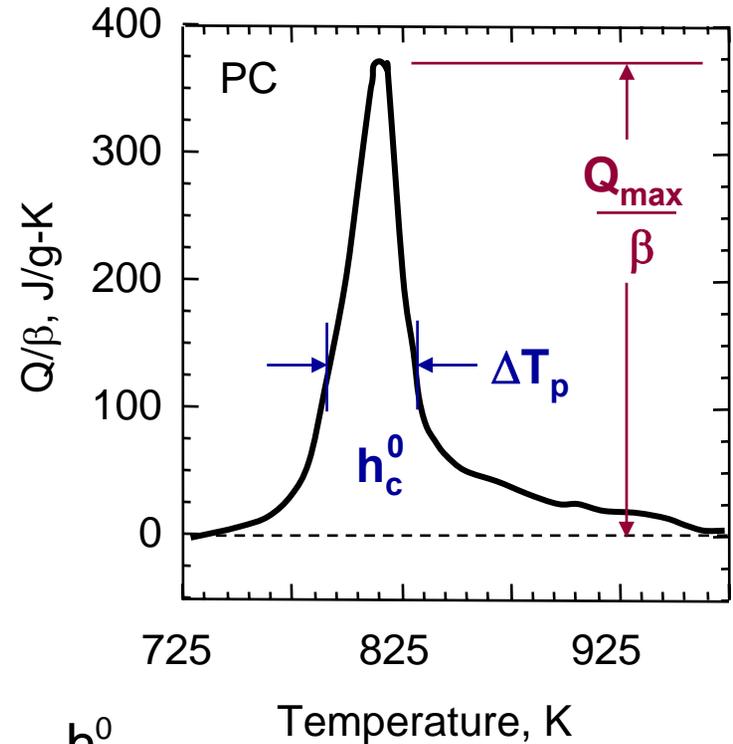
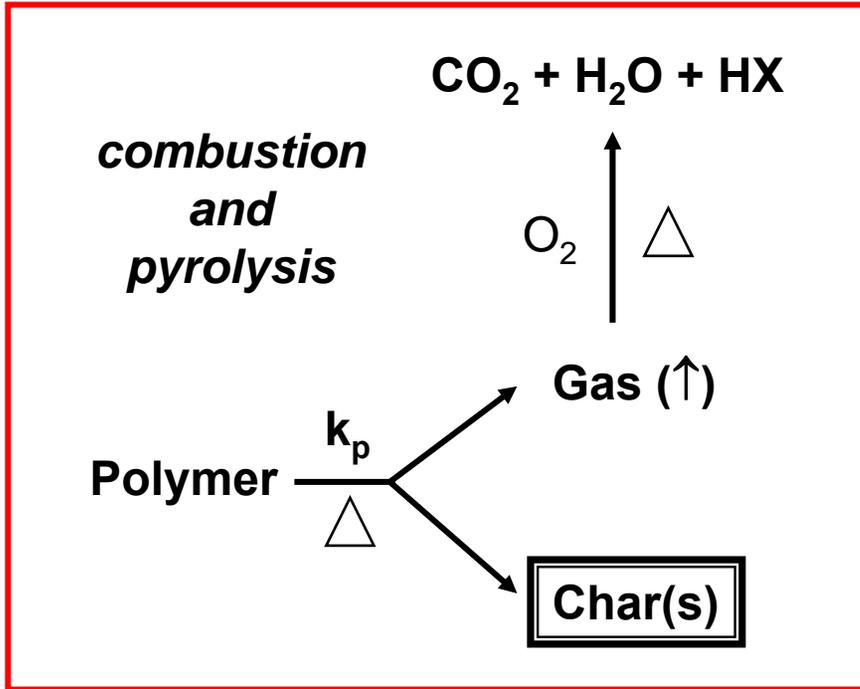
$$\text{Heat Release Capacity} \equiv \frac{\dot{Q}_c^{\max}}{\beta} = h_c^o \frac{(1-\mu)E_a}{eRT_p^2}$$

PCFC provides Heat Release (HR) Capacity as a material property and key parameter in determining flammability.

- h_c^o = Heat of combustion
- E_a = Activation energy
- μ = Char fraction
- T_p = T at peak mass loss
- R = gas constant
- \dot{Q}_c^{\max} = Peak heat release rate
- β = Heating rate

HEAT RELEASE RATE MODEL

*Rich Lyon, Rich Walters, Stanislav Stoliarov
Federal Aviation Administration*



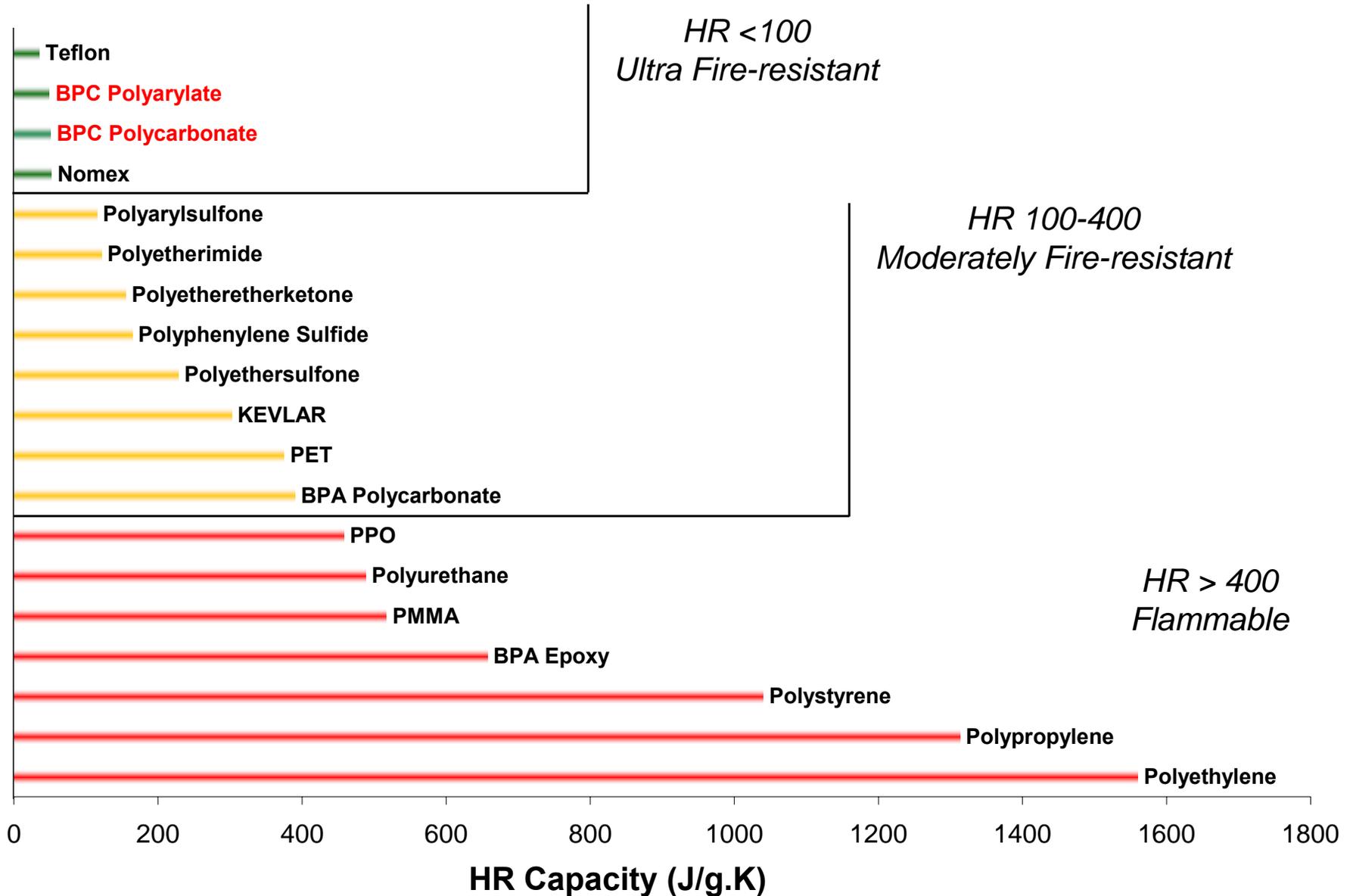
Heat Release Capacity: $\eta_c = \frac{Q_{\text{max}}}{\beta} = \frac{h_c^0}{\Delta T_p}$
(J/g-K)

Peak Height Method \uparrow

Peak Area Method \uparrow

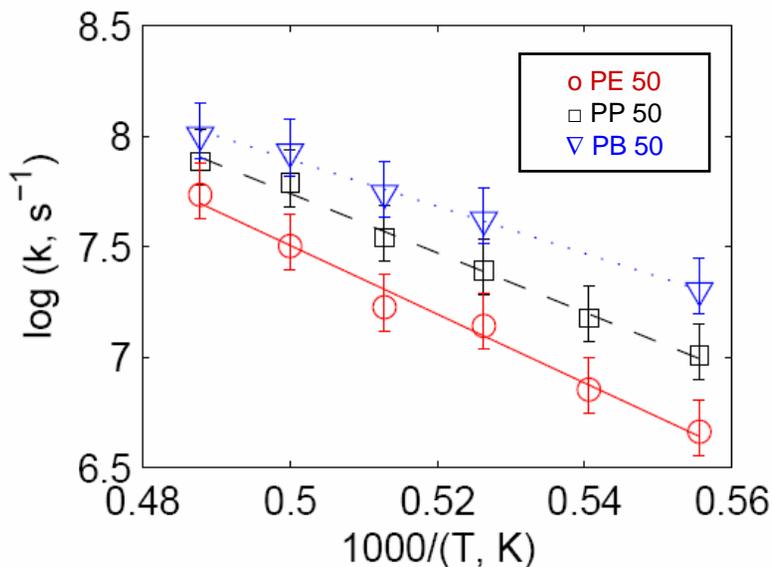
Heat Release Capacity of Polymers

Walters, R.N.; Lyon, R.E. *J. Appl. Polym. Sci.* **2003**, **87**, 548.



Reactive Molecular Dynamics to simulate polymer decomposition, and guide new polymer development: Ken Smith, PHil Westmoreland

- Developed a new reactive forcefield method, RMDff
- Developed a new Reactive Molecular Dynamics code, RxnMD
- Objective: Use microscopic reaction mechanisms to describe entire macroscopic polymer decomposition *a priori* via Kinetic Monte Carlo (KMC).

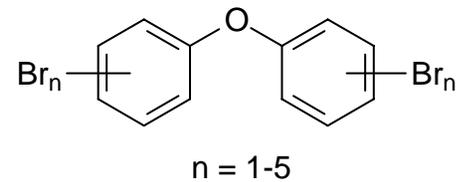
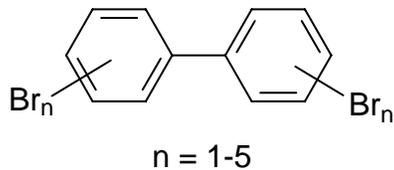


Polymer	$A \times 10^{15} (\text{s}^{-1})$	$E_A (\text{kJ/mol})$
PE 50	1.92	297.7
PP 50	0.289	257.3
PB 50	0.0159	203.2

Brominated anti-flammable additives

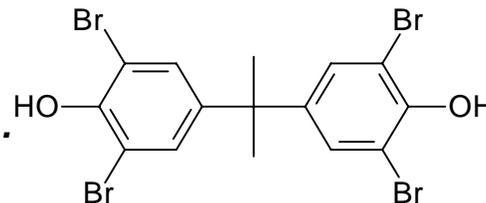
Halogenated additives, and halogenated polymers, give low flammability but are environmentally hazardous/questionable, and/or politically unfavorable

Polybrominated biphenyls (PBBs)



Problems: leaching from polymer, toxicity, environmental persistence

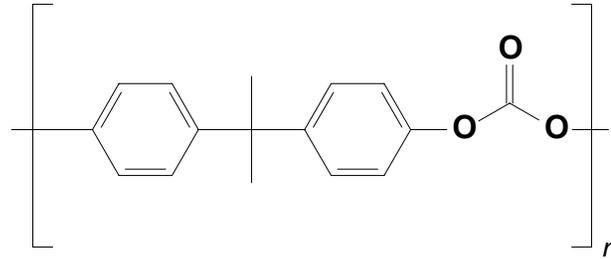
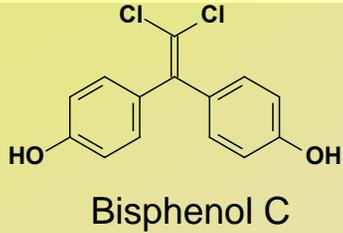
Brominated monomers for integration into polycarbonate, polyesters, polyethers, epoxies...



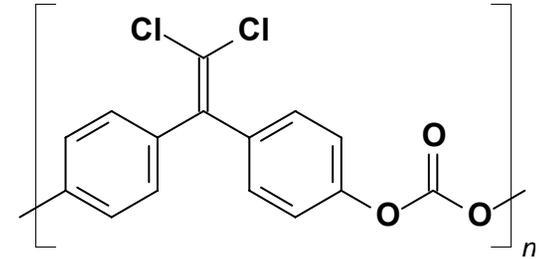
Clay-polymer and nanotube-polymer composites show flame resistance...

Challenge: new polymers with inherently low flammability but no halogen

Bisphenol C vs. Bisphenol A



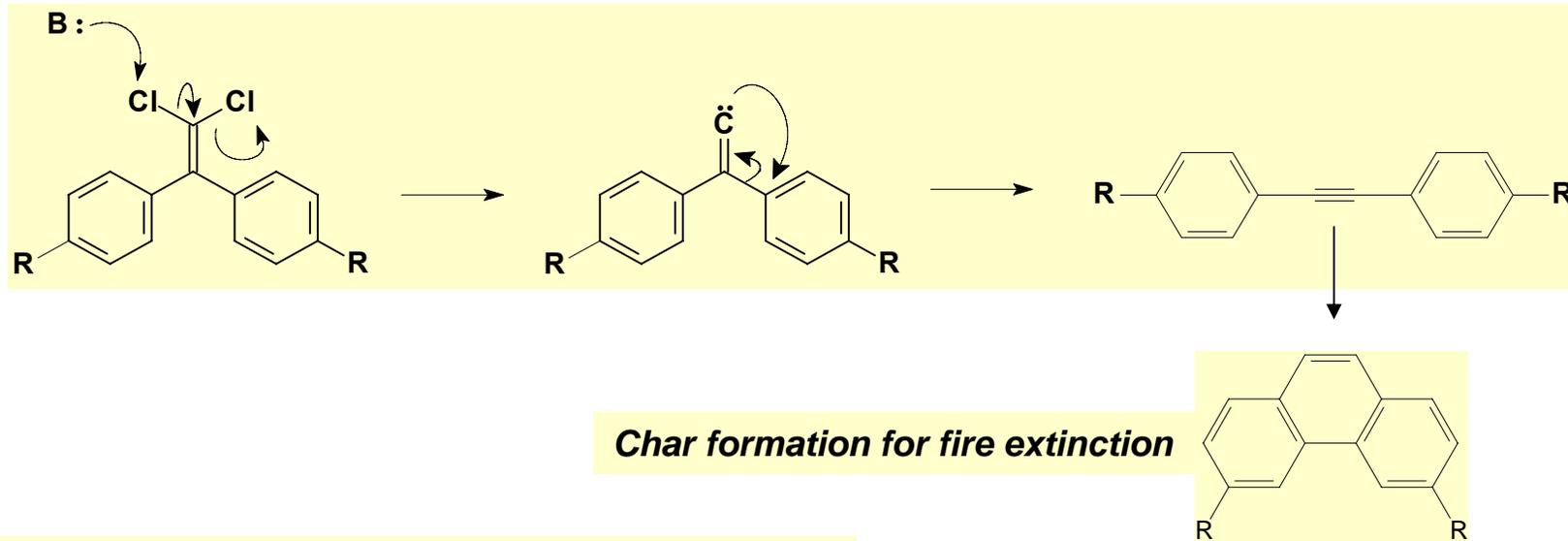
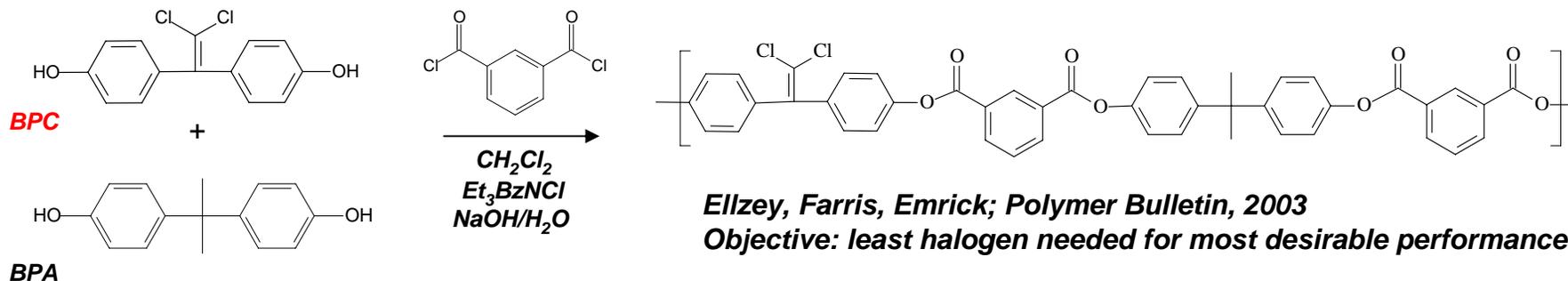
**Bisphenol A Polycarbonate
(Lexan)**



Bisphenol C Polycarbonate

Morphology	Amorphous	Amorphous
Tg (°C)	152	168
Flex Modulus (ksi)	336	376
Flex Strength (psi)	16,300	16,200
Tensile Yield Strain (%)	10	11
NBS Smoke (Dm)	165	75
Oxygen Index (%)	26	56
HR Capacity (J/g.k)	390	29

Bis-phenol C containing polymers

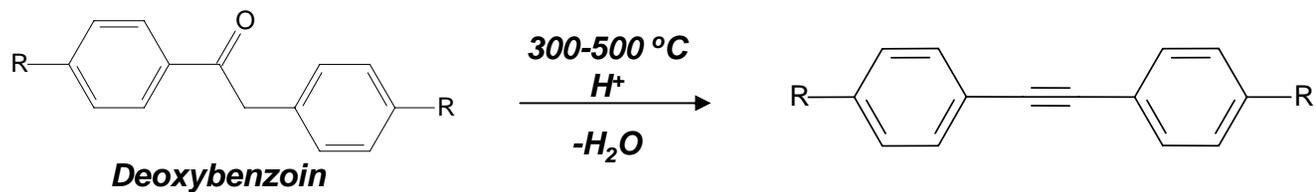


1. Chlorine content in BPC prevents widespread use;
2. Chlorine content in BPC may not be the key feature that leads to its anti-flammable properties; setting up rearrangement chemistry appears to be crucial

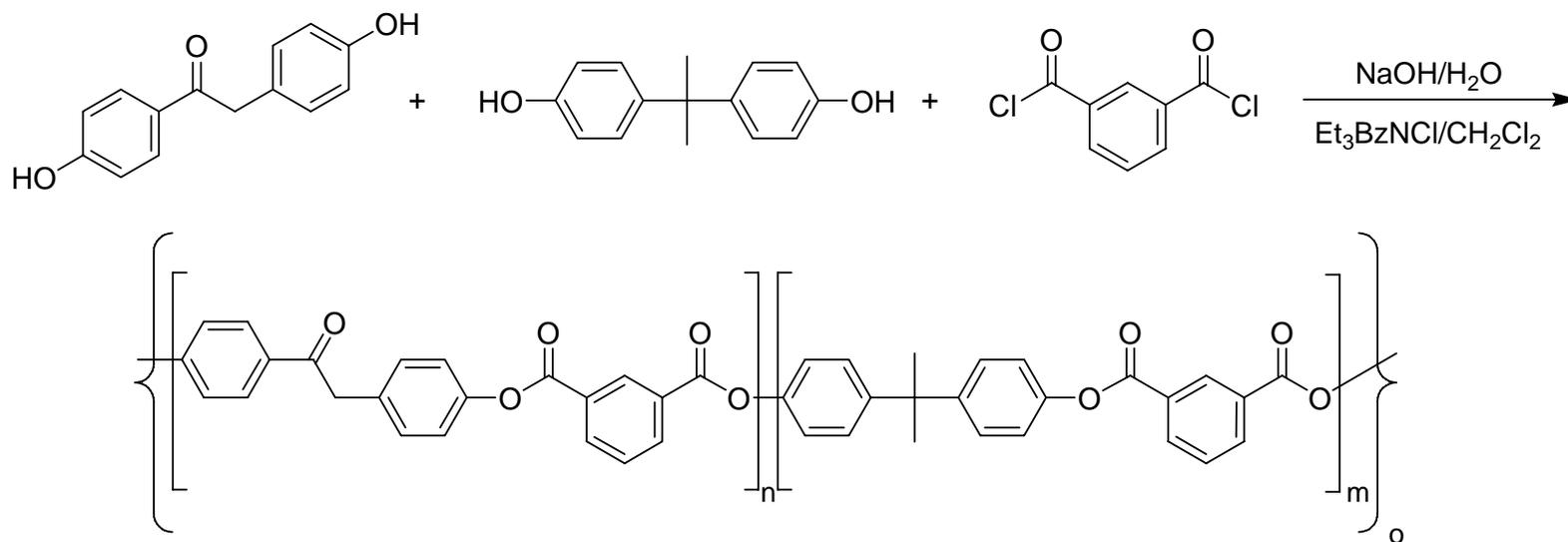
Ramirez, M. L. *Thermal Decomposition Mechanism of 2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethylene Based Polymers*. DOT/FAA/AR-00/42.; Department of Transportation, Federal Aviation Administration, National Technical Information Service: Springfield, VA, 2001;
 Stolorav, S.I.; Westmoreland, P.R. *Polymer* **2003**, *44*, 5469; van der Waals et al. *J. Mol. Cat. A* **1998**, *134*, 179

Halogen-free anti-flammable polymers

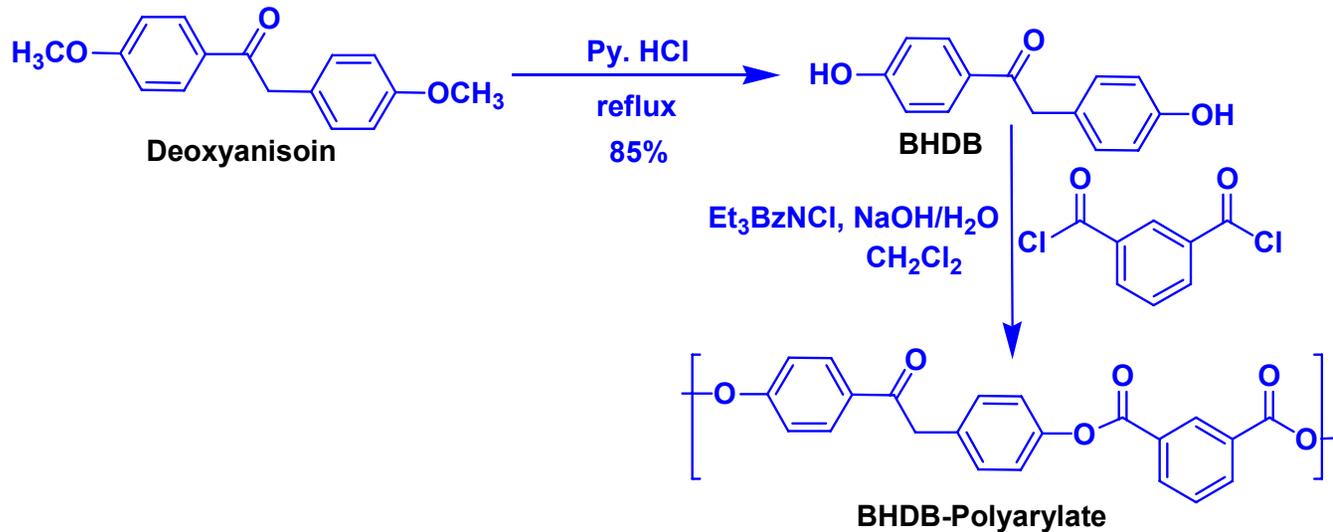
Deoxybenzoin-based polymers



van der Waals et al. J. Mol. Cat. A 1998, p.179



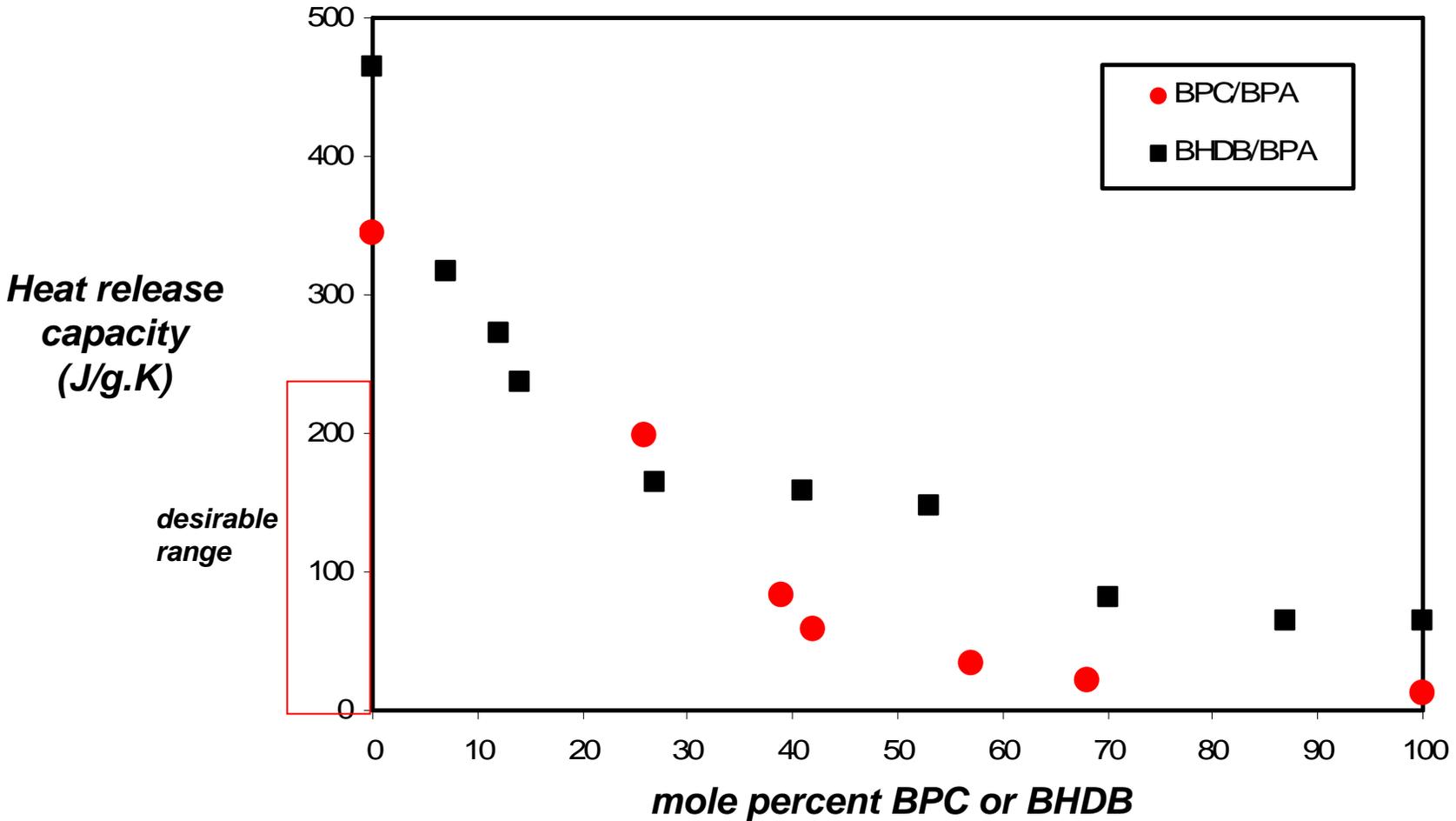
Deoxybenzoin-based Polyarylates



- Demethylation of desoxyanisoin gives 4,4'-bishydroxydeoxybenzoin (BHDB)
- **BHDB-polyarylate:**
 - Low solubility in common organic solvents
 - Relatively low molecular weights obtained (10-25K)
 - Use BPA as bisphenolic comonomer: increase solubility, increase flammability

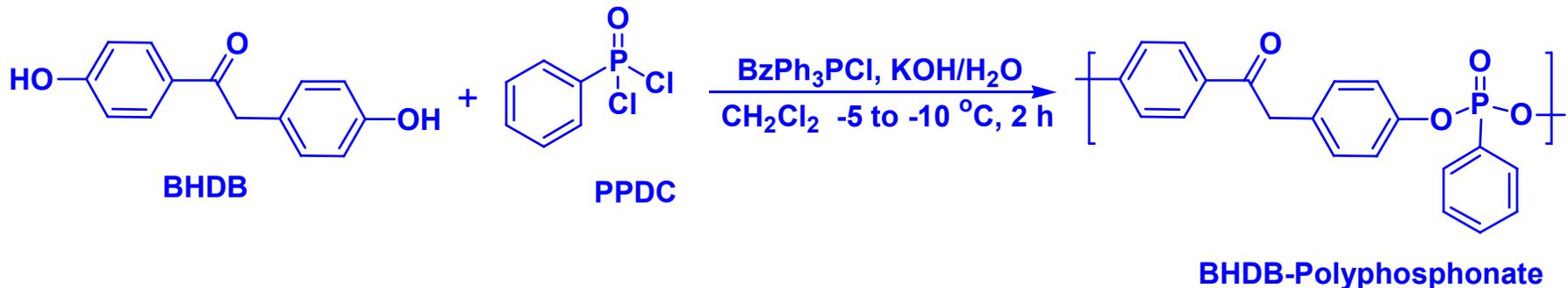
Performance of BPC vs. BHDB polymers

non-halogenated BHDB vs. *chlorinated bis-phenol C*



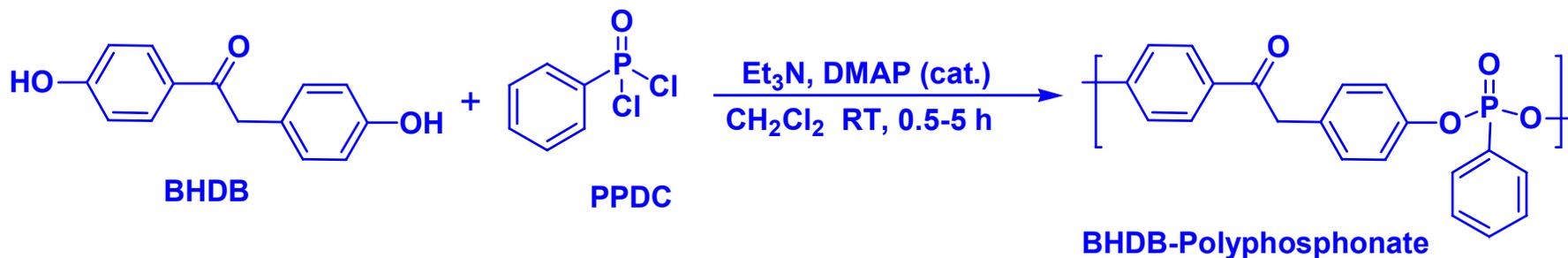
Synthesis of BHDB Polyphosphonates

Interfacial polymerization



- Soluble in most of common organic solvents like dichloromethane, chloroform, THF, DMSO, DMF etc.
- ^{31}P NMR: δ 12.7 ppm (-O-PO-O)
Three overlapping peaks due to regio-isomers (H-H, T-T and H-T)
- FT-IR: 1681 (ν_{CO}), 1269 ($\nu_{\text{P=O}}$), 1193 ($\nu_{\text{P-O-C}}$)
- GPC (DMF): $M_w=22300$ (PDI=2.6)

Solution polycondensation



End-capping Agent	Reaction Time(h) ^a	Yield (%)	GPC ^b		
			M _w	M _n	PDI
2,6-Me ₂ PhOH	0.5	79	53600	23600	2.27
2,6-Me ₂ PhOH	1	75	115800	39800	2.92
2,6-Me ₂ PhOH	2	78	140300	45800	3.06
2,6-Me ₂ PhOH	4	86	55400	23200	2.39
Phenol	2	75	138300	45500	3.05
Phenol	3	79	164900	43700	3.77
Phenol	5	80	52000	22200	2.34
Phenol ^c	3	75	5000	1900	2.64
None	3	77	74700	22700	3.29

^a Reactions were continued for another hour after the addition of end-capping agents;

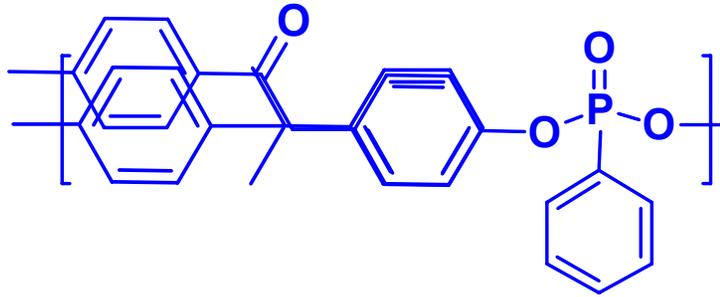
^b DMF as eluent against polystyrene standards; ^c Without catalyst.

- Anhydrous conditions
- End-capping to increase hydrolytic stability
- Phenol converts labile P-Cl bonds into more stable P-OPh bonds
- Catalyst helps to achieve high molecular weight

PCFC, TGA and DSC studies

- Heat Release Capacity = 80-100 J/g.K
- Char yield = 50-52%
- Decomposition temperature = 340-360 °C (5% weight loss)
- Glass transition temperature = 100-110 °C
- No melting point up to 300 °C

BHDB vs. BPA Polyphosphonates



Heat Release Capacity = 400-500 KJ/g.K
Char yield = 15%

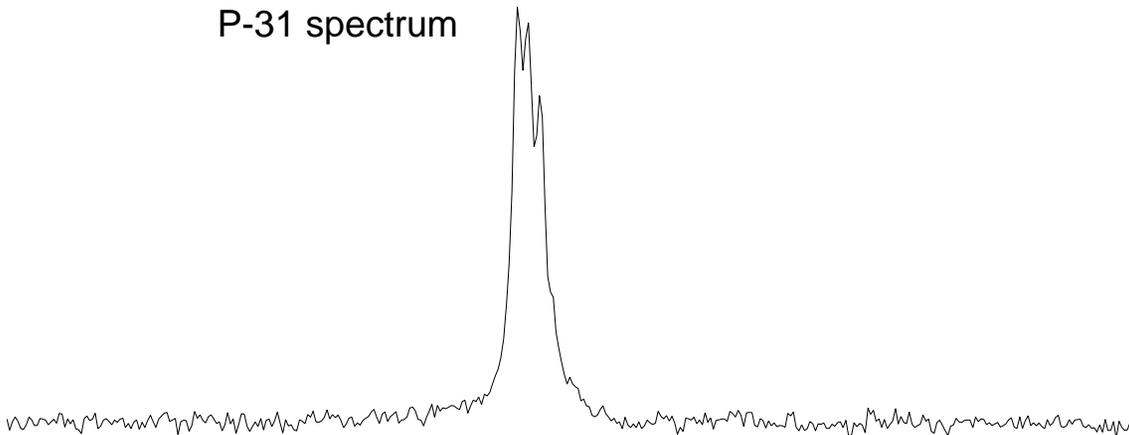
Flammability characterization: BHDB Vs BPA

Polymer	Bisphenol part	PCFC	TGA
		HRC (J/g-K)	Char yield (%)
Polyarylate	BPA	400	30
	BHDB	65	45
Polyphosphonate	BPA	450	20
	BHDB	80	52

- Choice of bisphenol part is key determinant of flammability
- Inherently fire-resistant properties evident when using deoxybenzoin unit

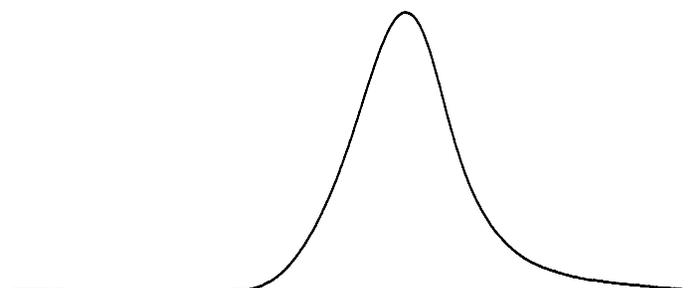
BHDB polyphosphonates

P-31 spectrum



Size exclusion chromatography

$M_w = 54,600$; $M_n = 24,100$
 $PDI = 2.27$

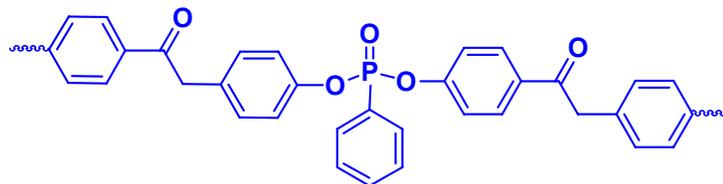


PPM 14.0 13.0 12.0 11.0

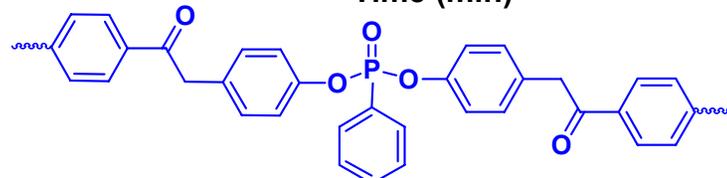
5 10 15 20 Time (min)



12.74 ppm (H-H)

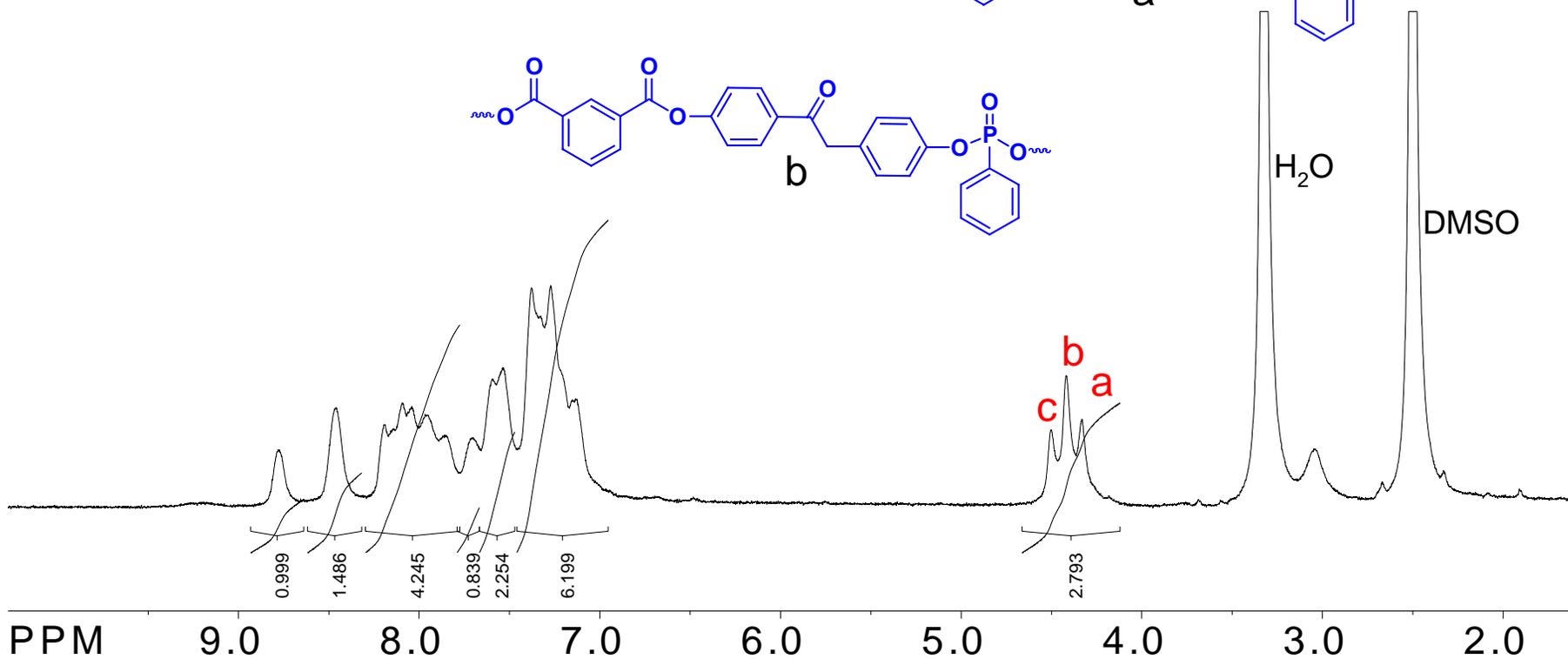
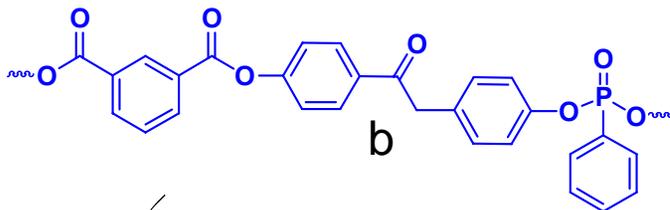
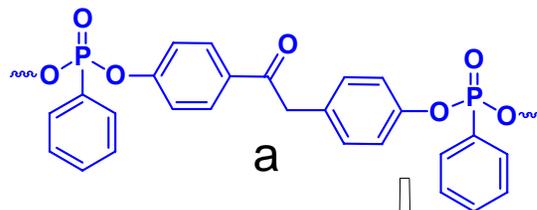
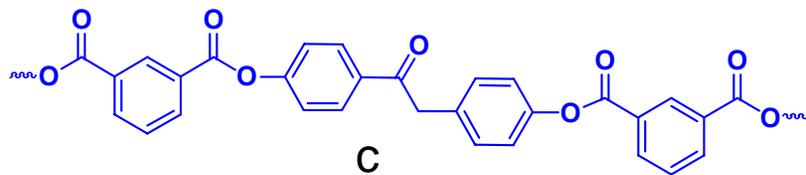


12.70 ppm (H-T)



12.64 ppm (T-T)

^1H NMR spectrum of BHDB polyphosphate/polyarylate copolymers



Molecular weight characterization

Isophthaloyl chloride: PPDC (molar ratios)		Yield (%)	GPC ^b		
Feed	Incorporated ^a		M _w (g/mol)	M _n (g/mol)	PDI
100:0	100:0	80	15,100	11,700	1.29
80:20	77:23	88	65,600	37,000	1.78
60:40	57:43	85	50,700	28,500	1.78
50:50	46:54	95	54,600	24,100	2.27
40:60	39:61	92	83,700	31,200	2.69
20:80	23:77	90	61,000	37,000	1.65
0:100	0:100	89	92,700	41,000	2.26

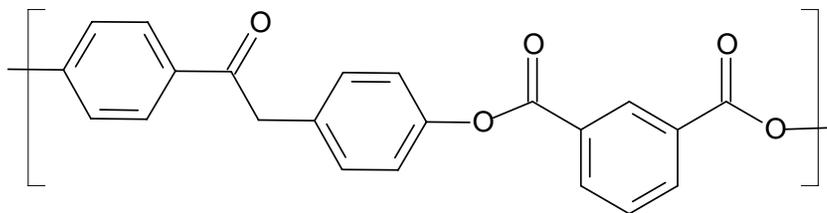
^a Calculated from ¹H NMR spectroscopy; ^b Using DMF as eluent, against polystyrene standards

Thermal and Flammability Studies

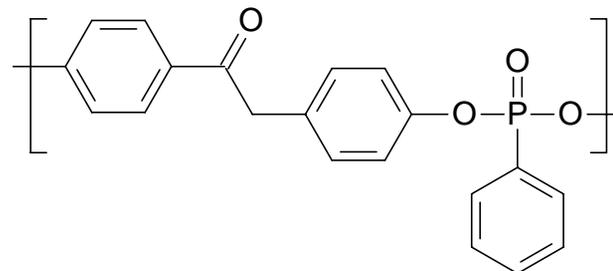
Isophthaloyl chloride: PPDC (molar ratios)	PCFC	TGA		DSC
	Heat release capacity (J/g-K)	5% Weight loss temperature (°C)	Char yield at 800 °C (%)	Glass transition temperature (°C)
100:0	65	340	45	157
77:23	48	346	50	142
57:43	41	383	56	133
46:54	36	367	54	131
39:61	40	390	57	124
23:77	59	394	55	110
0:100	80	397	52	100

- ❖ Phosphorus promote char formation efficiently in “oxygen-rich” polymers
- ❖ “Synergism” between phosphonate and isophthalate units

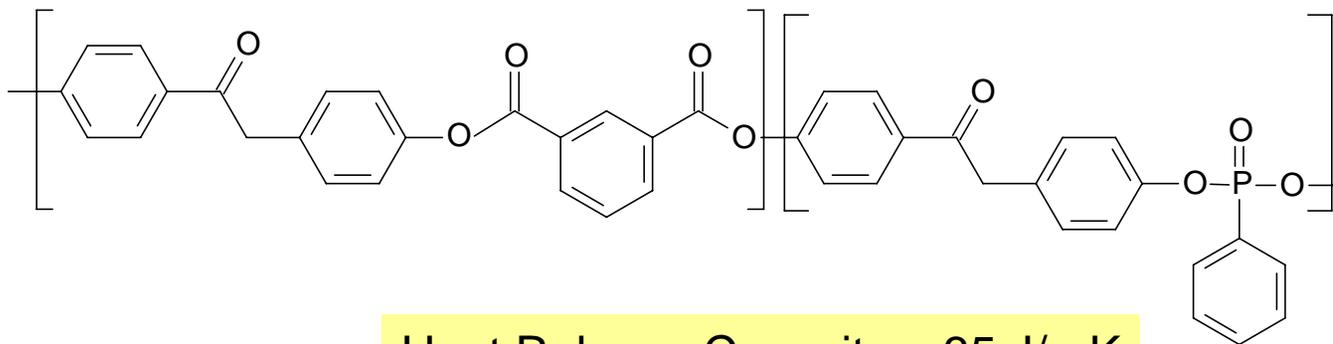
Summary: BHDB-containing polymers with low heat release capacity values



Heat Release Capacity = 65 J/g-K
Char yield = 45 %



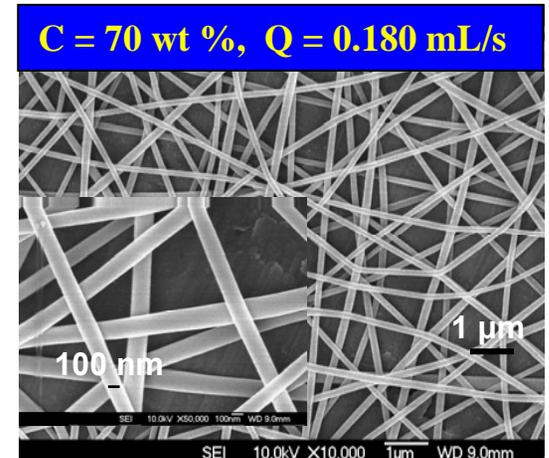
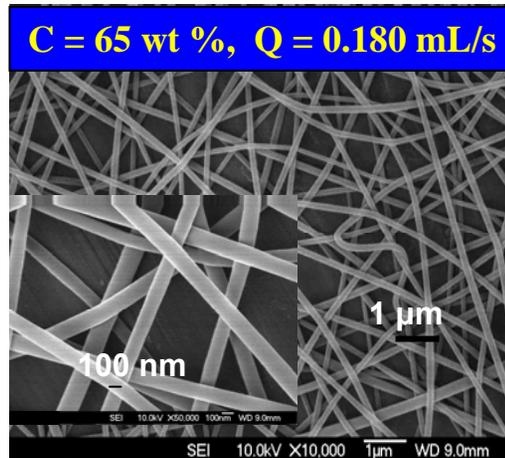
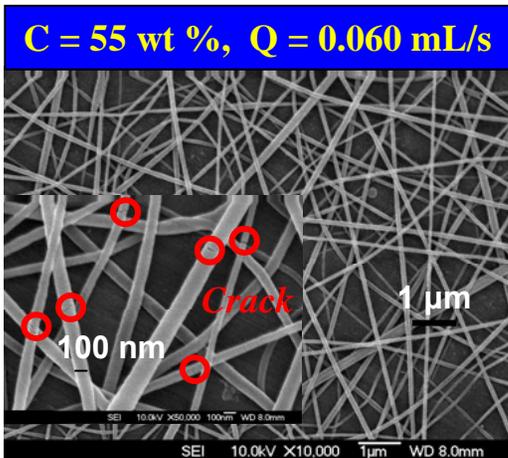
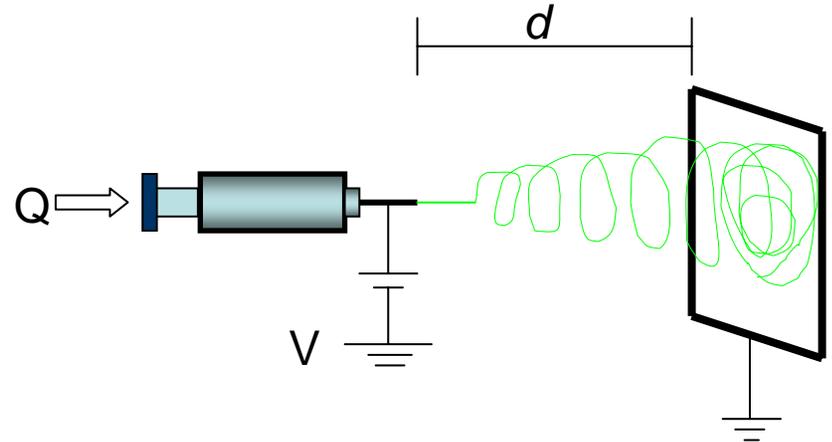
Heat Release Capacity = 80 J/g-K
Char yield = 52 %



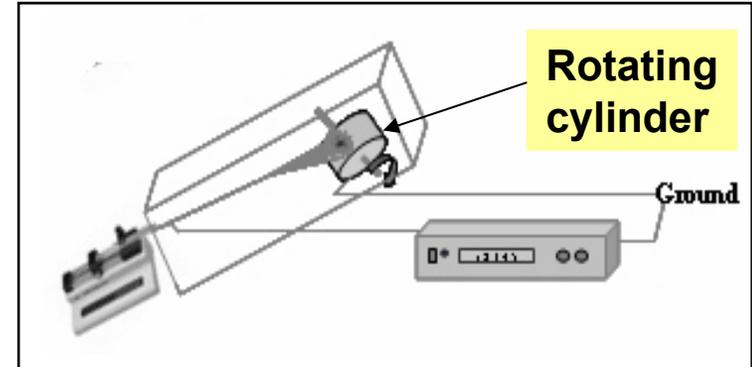
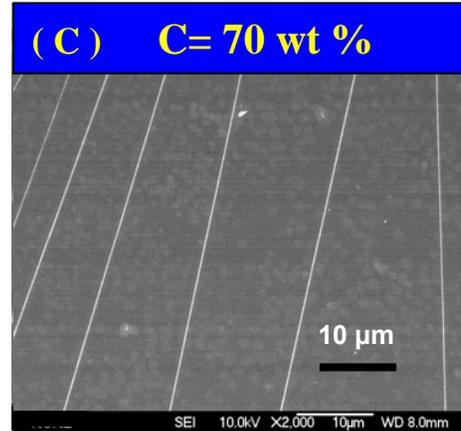
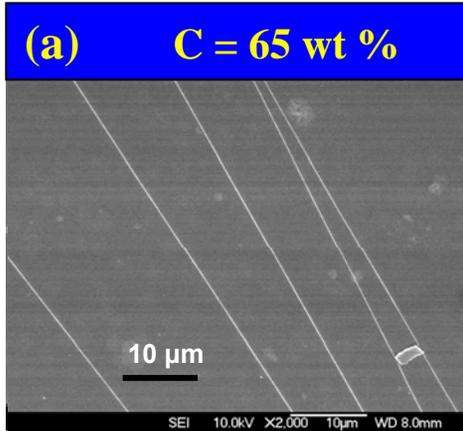
Heat Release Capacity = 35 J/g-K
Char yield = 57 %

Electrospun Nanofibers with BHDB polymers

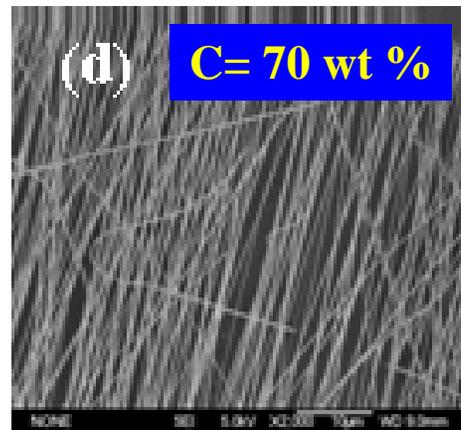
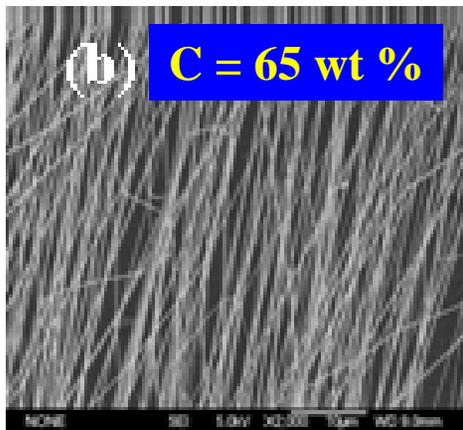
- Polymer : BHDB-polyphosphonate
- Molecular Weight: **44,700** (PDI = 3.28)
- Voltage (V) : **10 kV**, Solvent : **DMF**
- Flow Rate (Q): **0.06 ~ 0.18 mL/sec.**
- Polymer concentration (C): **55 ~ 70 wt %**
- Distance (d) between needle and target:**12 cm**



Oriented Electrospun Nanofibers



Rotating speed : **9.8 m/sec**



Wt (%)	Diameter (nm)
65	101 \pm 11
70	145 \pm 28

Properties of Electrospun Nanofibers

Heat Release Capacity (HRC)

Nanofibers: **70 ± 3 J/(g-K)** (SD = 6)

Diameter: **100 nm**, Mw: 44,700 (PDI = 3.28)

Polymer Powder: **80 ± 11 J/(g K)** (SD = 14)

T. Ranganathan et al., *Macromolecules*, 2006, 39, 5974



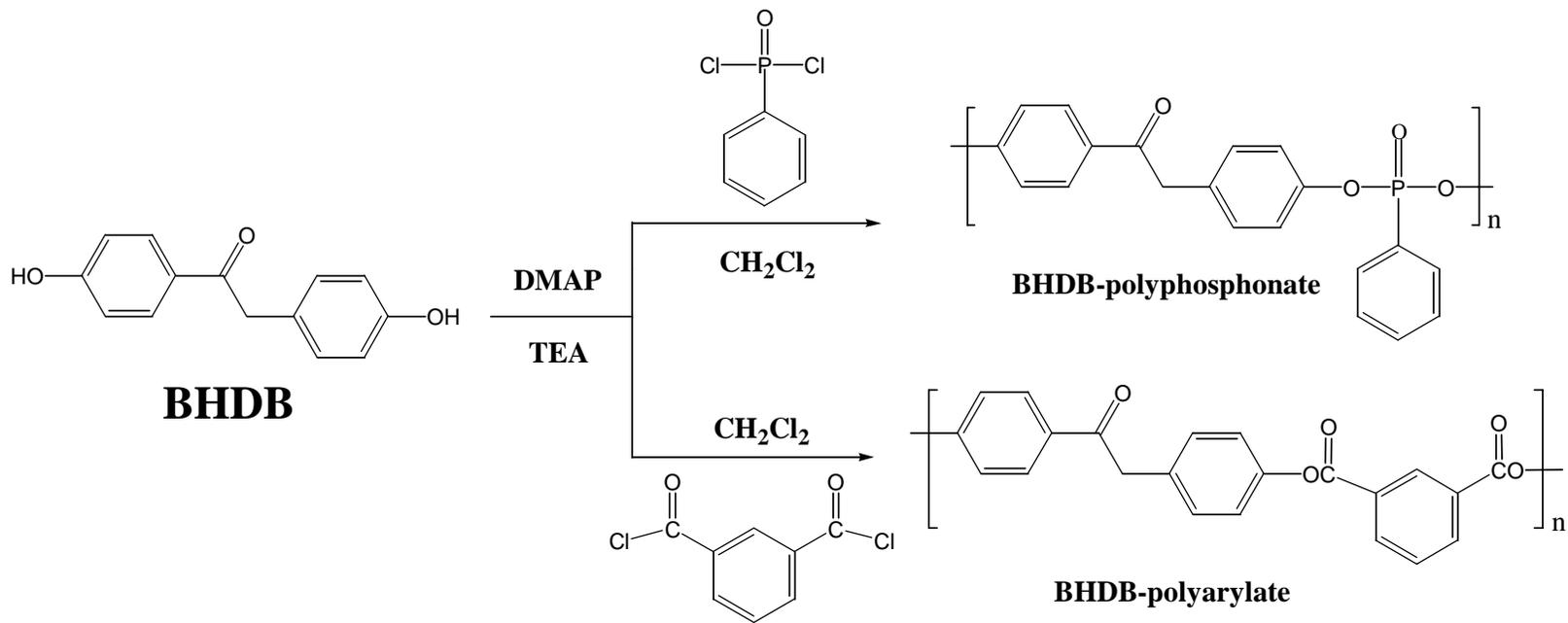
Mechanical Properties

	Mw (g/mol)	PDI	Tensile Strength @ Break (MPa)	Tensile Modulus (GPa)	Elongation @ break (%)
Fiber U ¹	69,500	2.29	50 ± 4	0.9 ± 0.1	113 ± 4
Fiber D ²	69,500	2.29	78 ± 2	2.9 ± 0.1	N/A
Cast Film	76,000	2.9	16.3 ± 2.7	1.49 ± 0.28	2.5 ± 1.7

- 1) Undrawn fiber (U)
- 2) 50 % drawn fiber (D)

density: 0.77 g/cm³, diameter: 588 ± 87 nm

BHDB-Polyphosphonate & arylate



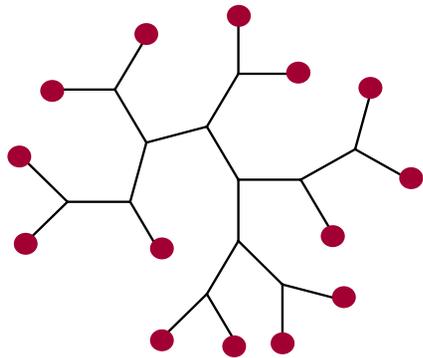
#	IPC: PPDC	Yield (%)	Solubility (mg/mL)	Solvent	GPC		
					M_w (g/mol)	M_n (g/mol)	PDI
1	0:100	90	700	DMF	44,700	13,600	3.28
2	100:0	64	< 3	DMSO	3,200	2,600	1.22

Summary and Future Directions

- **BHDB-polyarylates** showed excellent fire-resistant behavior (HRC ~ 65 J/g.K; Char yield ~ 45%); limited solubility in common organic solvents
- **BHDB-polyphosphonate** exhibited excellent solubility, while retaining flame-resistant properties (HRC ~ 80 J/g.K; Char yield ~ 52%)
- **BHDB-poly(arylate-co-phosphonate)s** showed HRC as low as ~35 J/g.K and char yield as high as ~57%
- Phosphorus acts efficiently in “oxygen-rich” polymers in promoting char formation
- Synthesis of BHDB polyarylate/phosphonate copolymers have been scaled up to >30 g, and mechanical properties are currently being studied

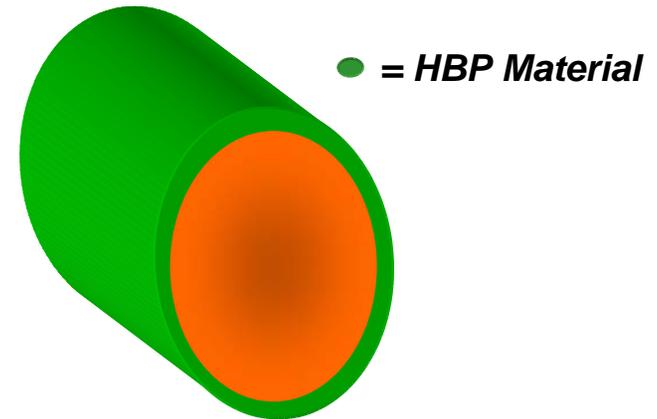
Application of hyperbranched polymers to flame-retardants

Hyperbranched polymers have been shown to migrate to polymer surfaces during co-extrusion processes



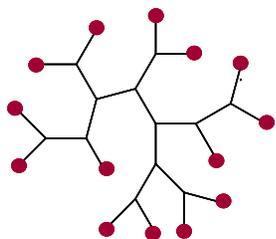
5% HBP

*Co-extrusion with
polymer of interest
(polyethylene,
polypropylene,
polystyrene, etc...)*

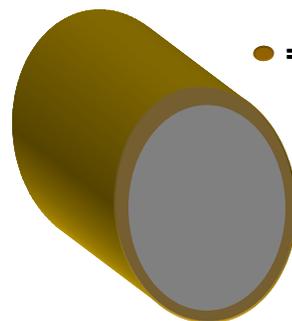


*Fiber cross-section showing
HBP coating on polymer surface*

Hyperbranched Polymer Flame-retardants



Extrusion
Bulk Polymer



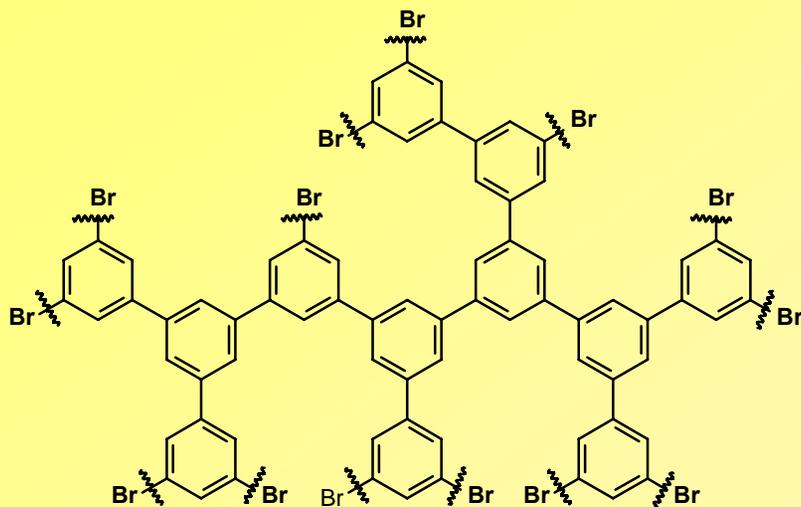
● = HBP Material

May be used to deliver functionality to surface

Hyperbranched Polymer (HBP)

Fiber Cross-Section showing HBP coating on surface

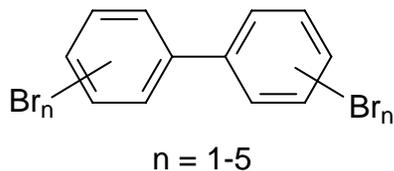
Mackay and coworkers, *J. Rheol.* **43**(3), 1999.



Hyperbranched Polyphenylene
(HBPP-Br)

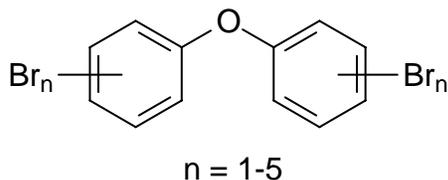
HR Cap (j/g.K)	6
THR (kJ/g)	0.7
Char Yield (%)	44

Halogenated Flame-retardants



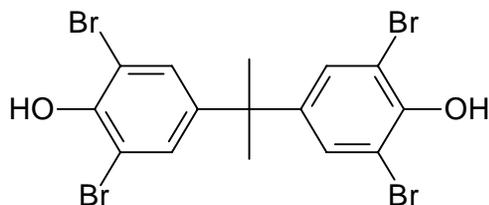
Polybrominated biphenyls (PBB's)

- *Environmentally persistent*
- *Lipophilic*
- *Toxic*
- *Banned worldwide*



Polybrominated diphenylethers (PBDE's)

- *Lipophilic; found in breast tissue*
- *Expected toxin*
- *May soon be banned*



- *Found in human blood samples in computer technicians*

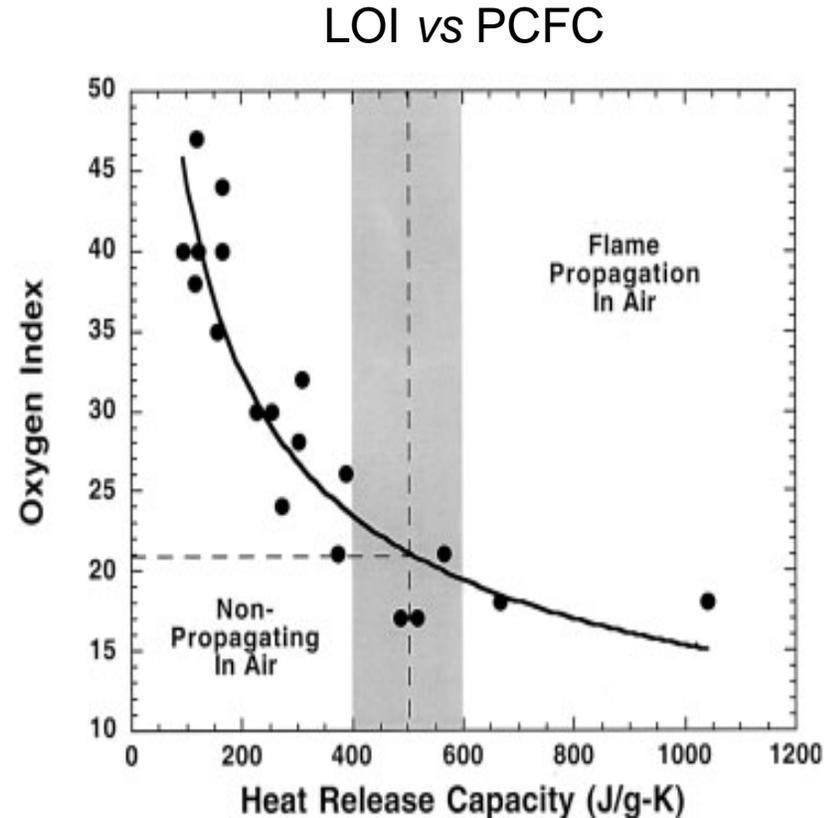
new flame-retardant materials needed

Background

- Flame Retardants (FR) are added to Polymers to
 - Increase resistance to ignition
 - Reduce flame spread
 - Suppress smoke formation
 - Prevent polymer from dripping
- Brominated FR additives
 - Very efficient and cost-effective
 - Leaching from polymer matrices
 - Environmental and health concerns
- Use of several polybrominated diphenyl ethers is restricted/banned in California, Michigan, and Oregon; others to follow...
- Non-halogenated FR, example Aluminum trihydrate (ATH)
 - Requires high loading (as high as 65%); affects mechanical properties of polymer products
 - Limitations in high processing temperatures

Flammability Characterization

- Traditional methods (~100g sample)
 - Cone calorimetry
 - UL-94 (vertical and horizontal)
 - Limiting oxygen index (LOI)
- **Pyrolysis combustion flow calorimetry (PCFC)**
 - Measures HRC, a material property that determines flammability
 - Correlates well with



Walters, R.N.; Lyon, R.E. *J. Appl. Polym. Sci.* **2003**, *87*, 548.

BHDB-Poly(arylate-phosphonate) copolymers

Polyarylate:

- ✓ Rigid, thermally robust aromatic ester backbone
- ✓ Excellent fire-resistant properties
- X Low solubility and moderately low molecular weight

Polyphosphonate:

- ✓ Good solubility
- ✓ Phosphorus improves char yield in “oxygen-rich” polymers

Copolymers:

- ✓ Combine the advantages of homopolymers
- ✓ Possible increment in char yield due to presence of two oxygen-rich species (deoxybenzoin and isophthalate units)
- ✓ Optimize phosphonate percent to improve solubility and processibility without diminishing mechanical properties

Synthesis of BHDB-Poly(arylate-co-phosphonate)s

